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Biological performance and trace organic contaminant removal by a side-stream ceramic nanofiltration membrane bioreactor

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Abstract
This study evaluated the performance of a side-stream ceramic nanofiltration membrane bioreactor (NF-MBR) system with respect to basic water quality parameters as well as trace organic contaminant (TrOC) removal efficiency. The results show a stable biological performance of the continuous NF-MBR system with high effluent quality (total organic carbon < 4 mg L-1 and NH4 +-N below the detection limit). Significantly higher performance by this NF-MBR in comparison to the conventional microfiltration/ultrafiltration MBR regarding the removal of a large number of TrOCs was observed. TrOC removal efficiency depended on their hydrophobicity and molecular features. All hydrophobic compounds (LogD pH=6 > 3) were well removed (>85%), except diazinon (59 ± 7%). Hydrophilic compounds containing electron donating groups were also well removed (>90%). By contrast, hydrophilic compounds containing electron withdrawing groups were poorly removed (8-54%). Most of the 40 TrOCs investigated in this study did not accumulate in the sludge. Only three hydrophobic compounds, namely amitriptyline, triclosan and triclocarban showed considerable accumulation in sludge (>500 ng g-1). Mass balance indicated biodegradation/transformation as the most significant TrOC removal mechanism by this NF-MBR.

Keywords
nanofiltration, membrane, bioreactor, performance, biological, trace, organic, contaminant, removal, side, stream, ceramic

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Abstract

This study evaluated the performance of a side-stream ceramic nanofiltration membrane bioreactor (NF-MBR) system with respect to basic water quality parameters as well as trace organic contaminant (TrOC) removal efficiency. The results show a stable biological performance of the continuous NF-MBR system with high effluent quality (total organic carbon < 4 mg L^{-1} and NH_4^+-N below detection limit). Significantly higher performance by this NF-MBR in comparison to the conventional microfiltration/ultrafiltration MBR regarding the removal of a large number of TrOCs was observed. TrOC removal efficiency depended on their hydrophobicity and molecular features. All hydrophobic compounds (Log$D_{pH=6}$ > 3) were well removed (>85%), except diazinon (59 ± 7%). Hydrophilic compounds containing electron donating groups (EDGs) were also well removed (> 90%). By contrast, hydrophilic compounds containing electron withdrawing groups (EWGs) were poorly removed (8 – 54%). Most of the 40 TrOCs investigated in this study did not accumulate in the sludge. Only three hydrophobic compounds, namely amitriptyline, triclosan and triclocarban showed considerable accumulation in sludge (>500 ng g^{-1}). Mass balance indicated biodegradation/transformation as the most significant TrOC removal mechanism by this NF-MBR.

Key words: Nanofiltration membrane bioreactor (NF-MBR), trace organic contaminants (TrOCs), molecular properties, biodegradation, sorption.

1. Introduction

Increasingly stringent environmental regulations and freshwater shortage are major drivers for introducing advanced water recycling technologies (Anderson et al., 2014). In recent years, membrane bioreactors have been widely used for wastewater treatment, in most cases, for subsequent water recycling (Anderson et al., 2014; Hai et al., 2014a; Li et al., 2015). Compared to the conventional activated sludge (CAS) process, membrane bioreactor (MBR) can be operated at a longer sludge retention time (SRT), higher mixed liquor suspended solid (MLSS) concentration, and with a much smaller physical footprint (Hai et al., 2014b). Thus, MBRs can offer a high effluent quality, which can be further purified for water reuse applications (Alturki et al., 2010; Pandey et al., 2014; Qin et al., 2006).

A challenging hurdle to water recycling is the widespread occurrence of trace organic contaminants (TrOCs) in municipal wastewater. Conventional wastewater treatment technologies were not designed for the removal of these TrOCs. As a result, effluent discharge is a major pathway for the introduction of TrOCs into the aquatic environment (Luo et al., 2014b). Uncertainty about potential health effects of chronic exposure to these TrOCs even at trace level has triggered the need for their removal during water reuse and wastewater treatment (Schwarzenbach et al., 2006).

MBR with key characteristics such as long SRT, high MLSS concentration has been considered as a promising technology for enhancing TrOC removal (Li et al., 2015; Navaratna et al., 2012). Several previous studies have compared TrOC removal between MBR and CAS. With respect to readily biodegradable TrOCs (*e.g.* caffeine and bezafibrate), MBR showed more stable removal performance than CAS (Sui et al., 2011). MBR also achieves better removal of certain TrOCs (*e.g.* trimethoprim, gemfibrozil, and metoprolol) that are moderately removed by CAS (15 – 80%). However, several persistent TrOCs (*e.g.* carbamazepine and diclofenac) were not sufficiently removed by both CAS and MBR (Bernhard et al., 2006; Sui et al., 2011). In addition, the removal efficiency of TrOCs by MBR can vary widely depending on their physiochemical properties (Tadkaew et al., 2011) as well as operating conditions such as SRT (Boonyaroj et al., 2012; Phan et al., 2014; Weiss and Reemtsma, 2008), temperature (Hai et al., 2011; Sui et al., 2011), hydraulic retention time (Fernandez-Fontaina et al., 2012) and mixed liquor pH (Sanguanpak et al., 2015; Tadkaew et al., 2010). More importantly, MBR alone is not sufficient for adequate removal of TrOCs for water reuse. As a result, MBR effluent is usually further polished by other advanced treatment processes such nanofiltration (NF) or reverse osmosis, UV oxidation, and

activated carbon adsorption prior to water reuse applications (Alturki et al., 2010; Nguyen et al., 2013; Qin et al., 2006).

To further enhance TrOC removal by MBR, several new configurations have been explored (Luo et al., 2014a). These include the integration of NF instead of the conventional microfiltration or ultrafiltration membrane with the biological reactor to form the NF-MBR configuration. Choi et al., (2007) reported the first NF-MBR study of municipal wastewater treatment in which they demonstrated excellent effluent quality of less than 4 mg L^{-1} in total organic carbon (TOC) content. However, previous studies have also showed several challenges in NF-MBR operation. They include salt accumulation in the biological reactor (Choi et al., 2007) and low permeate flux (< 2.5 L m^{-2} h^{-1}) (Choi et al., 2007; Zaviska et al., 2013). A key driver for developing NF-MBR is the capacity of the NF membrane to directly retain TrOCs or the macromolecules binding TrOCs (Fujioka et al., 2015; Nghiem and Hawkes, 2007), thus prolonging their retention time in the biological reactor for an enhanced removal. With the exception of the study by Zaviska et al. (2013), TrOC removal by NF-MBR has not been studied. Furthermore, Zaviska et al. (2013) investigated the removal of only ciprofloxacin and cyclophosphamide at 100 µg L^{-1} each. Thus a more systematic study covering compounds of diverse chemical compositions is required.

This study aims to evaluate the performance of an NF-MBR system with respect to basic water quality parameters as well as TrOC removal efficiency. The fate of 40 TrOCs during NF-MBR treatment was systematically evaluated and discussed.

2. Materials and methods

2.1 Trace organic contaminants

A set of 40 TrOCs was selected for investigation. These contaminants represent major TrOC groups (*e.g.* pharmaceutically active compounds, pesticides, industrial chemicals, and personal care products) of concern in domestic wastewater and surface water. They also cover a diverse range of physicochemical properties including molecular weight, hydrophobicity and chemical structure that allow for a systematic evaluation of the performance of membrane rejection and bioreactor. The hydrophobicity of the selected TrOCs was categorised according to the Log *D* value at the specific pH of operation. The presence/absence of electron donating group (EDG)/electron withdrawing group (EWG), nitrogen bearing cyclic structure were also examined to describe the biodegradability of TrOCs during biological treatment (Tadkaew et al., 2011). The compounds were purchased

from Sigma-Aldrich (Australia) with a purity of 99% or higher. A combined stock solution of TrOCs was prepared in methanol and stored at – 20 °C in the dark. TrOCs were spiked to the synthetic wastewater to achieve a final concentration of approximately 750 ng L^{-1} of each selected compound.

2.2 Laboratory scale NF-MBR set-up

A laboratory scale aerobic NF-MBR system was constructed for this study (Figure 1). The system consists of an aerobic bioreactor and a side-stream ceramic membrane module (Fraunhofer IKTS, Germany). The membrane module was 0.25 m in length with a total effective membrane area of 0.033 m^2. It has 7 channels with inner diameter of 6 mm. According to the manufacturer, this membrane has a mean pore size of less than 0.9 nm. Two peristaltic pumps (Masterflex L/S, USA) were used for recirculation and effluent extraction. The effluent extraction pump was operated on an 8 min on and 2 min off cycle. The on/off time aimed to reduce the stress of cross-flow intensity on biological flocs and to provide relaxation time to the membrane module. The reactor volume was maintained at 4 L using an automatic floating valve for feeding. An air pump was used to maintain dissolved oxygen content of 7 ± 1 mg L^{-1} in the bioreactor via a diffuser located at the bottom of the tank. Transmembrane pressure was monitored using two pressure gauges. The hydraulic retention time (HRT), temperature and mixed liquor pH were 27 h, 21.0 ± 2.6 °C, and 6.0 ± 0.5, respectively. A long HRT (corresponding to a permeate flux of 4.5 L m^{-2} h^{-1}) was applied in this system to maintain a relatively stable membrane flux and minimize membrane fouling so that the focus of the study could be maintained on the evaluation of the TrOC removal. Membrane cleaning was only conducted when the transmembrane pressure reached 40 kPa. A cross-flowrate of 1.2 L min^{-1} within the membrane module was maintained for fouling minimisation. The NF-MBR system was operated without sludge withdrawal except sampling for MLSS concentration measurement (approximately 0.5% total mass per week). During the period of TrOC addition, the system was covered with aluminium foil to prevent any photodegradation.

[FIGURE 1]

2.3 Experimental protocol

The NF-MBR system was inoculated with activated sludge obtained from the Wollongong Wastewater Treatment Plant (Wollongong, Australia). A medium strength municipal synthetic wastewater (TOC = 124 ± 16 mg/L, n = 26) was used to provide carbon, nitrogen,

phosphorus and trace metal ions for the growths of the microbes (Alturki et al., 2012). The synthetic wastewater was prepared daily by diluting a concentrated stock with deionized water. The concentrated stock solution was prepared weekly and stored at 4 °C. After 25 d of acclimatization, the NF-MBR achieved a stable biological performance as indicated by the stable removal efficiency of TOC and NH_4^+-N as well as MLSS concentration (Section 3.1). TrOCs then were introduced into the synthetic wastewater that was continuously fed to the system. Supernatant samples were collected from the mixed liquor by centrifuging (at 3000g) then filtering through 1 µm filter paper (Millipore, Australia). Over the last two weeks of the experiment, mixed liquor samples were collected to determine the fate of TrOCs in solid phase.

2.4 Analytical methods

2.4.1 Analysis of basic water quality parameters

Total organic carbon (TOC) and total nitrogen (TN) were analysed using a TOC/TN-V_{CSH} analyser (Shimadzu, Japan). NH_4^+-N and PO_4^{3-}-P concentrations were determined by flow injection analysis (Lachat instruments, Milwaukee, USA) based on the Standard Methods 4500-NH_3 H and 4500-P G, respectively. Anions (i.e. NO_2^--N and NO_3^--N) were measured using Ion Chromatography (IonPac AS23 Anion-Exchange Column, Dionex Corporation, USA). Measurement of MLSS and MLVSS concentrations in bioreactors were done according to the Standard Method 2540.

The concentrations of cations (i.e. Fe, K, Mg, and Na) were determined using an Agilent 710 inductively coupled plasma optical emission spectrometry (ICP-OES) system (Agilent Technologies, Australia).

2.4.2 Analysis of trace organic contaminants

Influent, mixed liquor and effluent samples (0.25 L) were collected for analysis of TrOC concentration. Mixed liquor samples were centrifuged and then filtered through 1 µm filter paper (Millipore, Australia). Aqueous samples were subjected to an analytical method previously reported elsewhere (Phan et al., 2015). Briefly, the isotope labelled surrogate stock solution was added to each sample to obtain a concentration of 200 ng L^{-1} for each surrogate standard. The aqueous samples were then extracted using 6 mL Oasis HLB solid phase extraction (SPE) cartridges (Waters, Milford, MA, USA) followed elution with methanol (10 mL) and methyl-t-butylether (5 mL). The solvent was removed by evaporation under nitrogen and reconstituted in methanol (1 mL). Analysis was performed using a high performance

liquid chromatograph (Agilent 1200 series, Palo Alto, CA, USA) coupled with tandem triple quadrupole mass spectrometer (API 4000, Applied Biosystems, Foster City, CA, USA) employed in both positive and negative electro-spray modes.

TrOC concentration in sludge was determined using a solvent extraction method described in Wijekoon et al., (2013). The sludge sample was freeze-dried using an Alpha 1–2 LD plus Freeze Dryer (Christ GmbH, Germany). The dried sludge (0.5 g) was extracted successively with 5 mL methanol and 5 mL dichloromethane - methanol (1:1v/v) by ultrasonic solvent extraction. The solvent was then evaporated using nitrogen gas and the extracts were diluted to 500 mL with Milli-Q water. The samples were then analysed as described above.

3. Results and discussion

3.1 Biological performance of a continuous NF-MBR

Stable biological performance of the NF-MBR system was achieved after 25 d of acclimatization. During the acclimatization period, MLSS decreased from 5.5 g L^{-1} to a stable value of 2.1 ± 0.5 g L^{-1} (n =16). The MLVSS/MLSS ratio was constant at around 0.8.

At the end of the acclimatization phase, TrOCs were continuously introduced to the influent solution at approximately 750 ng L^{-1} of each compound. The introduction of TrOCs to the influent solution did not result in any noticeable variation in the biological performance of the system (Figure 2).

Despite a low sludge concentration (MLSS of 2.1 ± 0.5 g L^{-1}), high TOC removal (>95%) was consistently achieved throughout the study (Figure 2). This TOC removal efficiency is significantly higher than those observed for conventional MBR employed MF/UF membrane (Phan et al., 2014; Wijekoon et al., 2013). The observed improvement in TOC removal performance can be attributed to the better retention capacity of the NF membrane. Indeed, 60% of suspended or colloidal/macromolecule bound TOC was removed by the NF ceramic membrane. The supernatant TOC in the reactor and the effluent TOC were 10 ± 4 mg L^{-1} and 4 ± 2 mg L^{-1}, respectively. In addition, the MLVSS/MLSS ratio was 0.8, which is similar to that in a typical biological reactor coupled with either MF or UF membranes.

Due to nitrification, near complete removal of ammonia was consistently observed throughout the experimental period after acclimatization (Figure 3). Nitrite concentration was either negligible or below the detection limit while nitrate concentration of around 32 mg L^{-1} was detected in the supernatant and effluent (Table 1). The results demonstrate that this NF-MBR system could sustain the development of slow growing autotrophic bacteria. As

196 expected, a low TN removal (23 ± 8%) was observed throughout the study (Figure 1). This is
197 due to the lack of anoxic condition in this system which is essential for denitrification
198 process. Similarly, no discernible biological phosphorus removal was observed (Table 1).
199 Biological phosphorus removal requires sequential exposure of activated sludge to aerobic
200 and anaerobic conditions followed by sludge withdrawal (Phan et al., 2014). Such
201 arrangement for nutrient removal was beyond the scope of this study.

202 **[FIGURE 2]**

203 **[FIGURE 3]**

204 The mixed liquor and effluent revealed similar conductivity (data not shown), indicating that
205 salts were not rejected by the ceramic NF membrane used in this system. This can also be
206 confirmed by examining the ionic composition of the influent, supernatant, and effluent
207 (Table 1). The results demonstrate that by deploying a relatively loose NF membrane (mean
208 pore size of 0.9 nm), ion rejection is negligible and salinity build-up in the bioreactor can be
209 avoided. As a result, stable biological performance of NF-MBR system was sustained. This
210 finding is in good agreement with a previous study by Zaviska et al., (2013).

211 **[TABLE 1]**

212 *3.2 TrOC removal*

213 In this study, TrOC concentrations in both supernatant of bioreactor mixed liquor and effluent
214 were measured to assess the role of NF membrane on TrOC rejection. Consistent with the
215 observation of low salt rejection, negligible TrOC rejection by the NF membrane was
216 demonstrated via similar values of TrOC concentrations between supernatant and effluent
217 (Figure 4). Additionally, there was no correlation between removal efficiencies and
218 molecular weight (MW) of TrOC compounds (Table 2). These results are consistent with the
219 large nominal pore size of 0.9 nm of this ceramic NF membrane. Nevertheless, this ceramic
220 NF membrane can offer a complete retention of suspended particulate matter and organic
221 aggregates. Given the adsorption of TrOCs to suspended particulate matter and macro-
222 organic molecules, an enhanced TrOC removal by the NF-MBR investigated here is still
223 apparent as can be seen below.

224 **[FIGURE 4]**

225 Overall, stable TrOC removal was observed in this study although the removal efficiency of
226 each individual compound varied significantly (Figure 4). The latter is probably governed by
227 the physiochemical properties of each specific TrOC.

228 All hydrophobic TrOCs (*i.e.* log $D_{pH=6}$ > 3) were removed by more than 85%, with diazinon
229 being the only exception (59 ± 7%). The observed high removal of hydrophobic TrOCs is
230 consistent with the literature (Table 2) and can be explained by their adsorption to sludge
231 particles. It is also noteworthy that the removal efficiencies reported here are within the upper
232 range when compared to values from conventional MBR systems (Table 2). A
233 comprehensive literature review by Luo et al (2014b) showed that diazinon is highly
234 persistent to aerobic treatment (Luo et al., 2014b). On the other hand, up to 90% removal of
235 diazinon by an anaerobic MBR has been reported by Wijekoon et al., (2015). They attributed
236 this removal efficiency of diazinon by anaerobic MBR to the presence of N/S in the
237 compound molecular structure which renders it susceptible to activity of nitrogen/sulphur-
238 reducing bacteria (Wijekoon et al., 2015). Diazinon removal by aerobic MBR has not been
239 reported in the literature. Nevertheless, several bacterial strains can facilitate the degradation
240 of diazinon leading to the formation of diazoxon and oxypyrimidine due to the hydrolysis of
241 the ester bond (Abo-Amer, 2011).

242 Given their diverse molecular structure and functional groups, the removal of hydrophilic
243 TrOCs (*i.e* log$D_{pH=6}$ < 3) varied significantly (Table 2). Results reported here are consistent
244 with the qualitative frame-work for prediction of TrOC removal by aerobic MBR proposed
245 by Tadkaew et al. (2011). Of the 40 TrOCs investigated in this study, 13 compounds
246 (dichloroprop, dilantin, meprobamate, primidone, TCEP, carbamazepine, simazine, DEET,
247 atrazine, diuron, diclofenac, diazepam and linuron) were poorly removed (8 – 54%). The low
248 removal efficiency of these 13 TrOCs can be explained by the presence of EWGs (e.g. –Cl
249 and -CONR) in their molecular structures that renders these compounds less susceptible to
250 oxidative metabolism (Tadkaew et al., 2011).

251 Results from this aerobic NF-MBR are also in good agreement with the literature. TrOCs
252 with EWGs in their molecular structure are well known for their persistence to
253 biodegradation. Removal of some compounds such as primidone, carbamazepine, DEET,
254 diuron and diclofenac were reported to significantly vary (Table 2). Biodegradation of these
255 persistent compounds may only occur under specific conditions such as stable nitrifying
256 condition (Suarez et al., 2010; Wijekoon et al., 2013) or combination of different redox
257 conditions (Phan et al., 2015; Stasinakis et al., 2009) that flourish the development of specific

258 microbial community and/or a distinct enzymatic profile. The removal of simazine has been
259 only reported by Alturki et al., (2012) who studied the performance of an osmotic MBR. It is
260 noted that the removal value reported by Alturki et al., (2012) was lower than that by our NF-
261 MBR. As noted by Alturki et al., (2012) salinity build-up was significant in their osmotic
262 MBR. By contrast, the salinity build-up was insignificant in our NF-MBR. Finally, this study
263 reported for the first time the removal of dichlorprop by an aerobic treatment process. Zipper
264 et al., (1999) has previously reported the biodegradation of dichlorprop by aerobic activated
265 sludge but only in batch tests.

266 Of the 17 hydrophilic TrOCs containing EDGs in their molecular structure, 14 compounds
267 were removed by more than 90%. These compounds include bisoprolol, caffeine,
268 sulfamethoxazole, paracetamol, enalapril, carazolol, fluoxetine, ketoprofen, hydroxyzine,
269 amitriptyline, naproxen, ibuprofen, clozapine and gemfibrozil. These removal efficiencies are
270 at the upper end of the range reported in literature for these compounds (Table 2). The
271 presence of EDGs (-NH_2, -OH, -OR, -COR, -R) in molecular structure of these compounds
272 makes them more amenable to biodegradation. Degradation kinetic studies have
273 demonstrated high biodegradtionof paracetamol, caffeine, naproxen, gemfibrozil,
274 sulfamethoxazole, and ibuprofen (Abegglen et al., 2009; Joss et al., 2006).

275 In particular, as noted above and can be seen in Table 2, higher removal efficiencies by this
276 NF-MBR compared to values from conventional MBR systems can be observed for many of
277 these hydrophilic TrOCs such as fluoxetine (85% *vs.* 26%) and clozapine (97% *vs.* 85%). The
278 removal of bisoprolol has only been reported in the literature by the conventional activated
279 sludge process (28 -72%) (Golovko et al., 2014) and the value was lower than the removal by
280 NF-MBR (88 ± 6%) in the current study. Complete biomass retention and long sludge
281 retention time can be an advantage of this NF-MBR system leading to improvement for
282 removal of certain TrOCs.

283 Three compounds (trimethoprim, triamterene and omeprazole) were moderately removed (42
284 - 65%) by this NF-MBR system. The removal efficiencies of trimethoprim, triamterene and
285 omeprazole by aerobic UF-MBR were 17, 28 and 62%, respectively (Tadkaew et al., 2011).
286 Trimethoprim is known to be resistant to biodegradation and may require a specific microbial
287 community or enzymatic profile (*i.e.* nitrifying community) for their biodegradation (Pérez
288 et al., 2005). On the other hand, very limited information regarding biodegradation of
289 triamterene and omeprazole is available. No further classification can be assigned to these

three compounds. Nevertheless, as a notable distinction, these three compounds have a nitrogen-bearing heterocyclic structure.

[TABLE 2]

3.3 Sorption on sludge and fate of TrOCs

In this study, photolysis was prevented by covering the system with aluminium foil (Section 2.2). All TrOCs investigated here have negligible volatility. Biodegradation and biosorption were previously considered as main removal mechanism of TrOCs by MBR (Phan et al., 2014; Wijekoon et al., 2013). To clarify the removal mechanism of TrOCs by this NF-MBR, sorption of TrOCs on sludge was monitored. Two sampling events (6 samples) were carried out at the last two weeks of experimental period to avoid the impact of lost sludge on the system performance.

Of the 40 TrOCs investigated here, 19 compounds were detectable in the sludge phase at the end of the experiment. Amongst them, seven compounds (i.e. triamterene, carazolol, verapamil, amitriptyline, linuron, triclosan and triclocarban) showed concentrations over 100 ng g^{-1} (Figure 5). Triamterene, carazolol, verapamil and linuron were present at concentrations within the range of 100 – 200 ng g^{-1}. Adsorption to the solid phase and resistance to biodegradation may lead to the temporary accumulation of these TrOCs in sludge. Three compounds (amitriptyline, triclosan and triclocarban) were accumulated in sludge at significant concentrations (576 ± 23, 833 ± 54 and 1006 ± 124 ng g^{-1}, respectively). The high sorption onto sludge of these three compounds was attributed to their very high hydrophobicity. Triclosan and triclocarban have Log*D* at pH 6 of 5.34 and 6.14, respectively. Hydrophobicity of amitriptyline changes significantly with pH. For example, it shows a Log*D* of 3.21, 2.28 and 1.57 at pH 8, 7 and 6, respectively. Its hydrophobicity and resistance to biodegradation possibly resulted in accumulation of amitriptyline in sludge that was also observed in previous studies (Phan et al., 2014; Wijekoon et al., 2015). Other hydrophobic compounds such as phenylphenol, bisphenol A, t-octylphenol, nonylphenol showed little or no accumulation in sludge, indicating their high biodegradation by the system.

[FIGURE 5]

To further clarify the fate of TrOCs during NF-MBR treatment, the mass balance of each compound was calculated based on the total amount in influent, effluent and sludge. For well removed TrOCs, biodegradation/transformation was found to play the most important role for their removal by the system (Figure 6) as also reported in case of MF/UF-MBR (Phan et al.,

2014; Wijekoon et al., 2013). It is noted that this NF-MBR system was operated at low MLSS concentration with minimum sludge withdrawal. Accordingly, contribution of sorption on sludge was negligible for most of the compounds. Even for the compounds showing significant concentration in sludge (e.g. amitriptyline, triclosan and triclocarban), the contribution of sorption on sludge to their overall fate was insignificant (2 – 4%). This result demonstrated that NF membrane can be applied to develop an NF-MBR with high biodegradation capacity.

[FIGURE 6]

4. Conclusions

Stable biological performance and high effluent quality were obtained with a ceramic NF-MBR system. Higher removal efficiencies by this NF-MBR compared to conventional MF/UF MBR were observed for a large number of TrOCs. TrOC removal efficiency was dependent on their physiochemical properties (hydrophobicity and the presence of EDGs or EWGs in the molecular structure). All hydrophobic compounds (Log*D* at pH 6 > 3.2) were well removed. Hydrophilic compounds containing only EDGs were also well removed, whereas hydrophilic compounds harbouring EWGs were poorly removed. Significant accumulation in the sludge phase was only observed for three hydrophobic TrOCs, namely amitriptyline, triclosan and triclocarban. Mass balance showed that biodegradation/transformation was the most important removal mechanism of TrOCs by this NF-MBR.

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Table 1: Concentration of elements and anion in NF-MBR in mg L^{-1} (average ± standard deviation of 14, 25, and 20 samples for each individual element, PO_4^{3-}-P and NO_3^--N, respectively). Supernatant samples were collected from the mixed liquor by centrifuging (at 3000g) then filtering through 1 µm filter paper.

Samples	Fe	K	Mg	Na	PO_4^{3-}-P	NO_3^--N
Influent	3	7 ± 1	4	54 ± 1	21 ± 4	-
Supernatant	3	8 ± 1	3 ± 1	50 ± 7	22 ± 5	33 ± 2
Effluent	0	7± 1	3 ± 1	47 ± 7	21 ± 3	32 ± 4

Table 1: Effect of physicochemical properties on removal efficiencies of the selected TrOCs (n = 20 and 30 for bioreactor and overall, respectively) in this study and corresponding values from literature (EDG = electron donating group; EWG = electron withdrawing group; MW = molecular weight).

Groups	Compounds	Log *D* at pH = 6	MW (g/mol)	This study (%)		Literature (%) [min – max]	References
				Bioreactor	Overall		
Log D < 3.2	*Compounds containing strong EWG and showing low removal efficiency*						
	Dichlorprop	-0.13	235.1	48 ± 38	54 ± 36	-	(Zipper et al., 1999)
	Dilantin	0.63	252.3	9 ± 6	10 ± 15	0 - 12	(Tadkaew et al., 2011)
	Meprobamate	0.7	218.3	10 ± 6	12 ± 8	15	(Tadkaew et al., 2011)
	Primidone	0.83	218.3	26 ± 25	28 ± 25	0 - 98	(Phan et al., 2015; Tadkaew et al., 2011; Wijekoon et al., 2013)
	TCEP	1.47	285.5	6 ± 5	8 ± 9	0	(Luo et al., 2014b)
	Carbamazepine	1.89	236.3	17 ± 8	18 ± 9	0 - 56	(Phan et al., 2015; Tadkaew et al., 2011; Wijekoon et al., 2013)
	Simazine	2.28	201.7	26 ± 18	27 ± 18	0	(Alturki et al., 2012)
	DEET	2.42	191.3	39 ± 8	45 ± 7	0 - 99	(Phan et al., 2015; Tadkaew et al., 2011)
	Atrazine	2.64	215.7	14 ± 18	16 ± 17	0 - 40	(Phan et al., 2014; Tadkaew et al., 2011; Wijekoon et al., 2013)
	Diuron	2.68	233.1	21± 12	23 ± 13	28 - 98	(Phan et al., 2015)
	Diclofenac	2.72	296.2	28 ± 27	45 ± 25	0 - 87	(Phan et al., 2015; Tadkaew et al., 2011; Wijekoon et al., 2013)
	Diazepam	2.8	284.7	9 ± 11	12 ± 12	17 - 42	(Suarez et al., 2010; Trinh et al., 2012)
	Linuron	3.12	249.1	32 ± 6	34 ± 9	21	(Tadkaew et al., 2011)
	Compounds containing only EDG and showing high removal efficiency						
	Atenolol	-2.63	266.3	76 ± 15	81 ± 5	70 - 97	(Phan et al., 2015; Tadkaew et al., 2011)
	Salicyclic acid	-1.45	182.2	70 ± 12	70 ± 19	88 - 99	(Phan et al., 2014; Wijekoon et al., 2013)
	Bisoprolol	-1.07	325.4	83 ± 11	83 ± 10	28 - 72	(Golovko et al., 2014)
	Caffeine	-0.63	194.2	99 ± 2	100 ± 1	50 - 99	(Phan et al., 2015; Tadkaew et al., 2011)
	Sulfamethoxazole	0.43	253.3	90 ± 4	93 ± 3	52 - 92	(Phan et al., 2015; Tadkaew et al., 2011)

	Paracetamol	0.48	151.2	100 ± 0	100 ± 0	95 -100	(Phan et al., 2015; Tadkaew et al., 2011)
	Enalapril	0.6	376.5	100 ± 0	100 ± 0	97	(Tadkaew et al., 2011)
	Carazolol	0.64	298.4	84 ± 7	83 ± 8	-	-
	Fluoxetine	0.88	309.3	85 ± 8	80 ± 10	26	(Trinh et al., 2012)
	Ketoprofen	1.14	252.3	92 ± 9	94 ± 7	44 - 95	(Phan et al., 2014; Tadkaew et al., 2011; Wijekoon et al., 2013)
	Verapamil	1.29	454.6	81 ± 15	69 ± 13	88	(Tadkaew et al., 2011)
	Hydroxyzine	1.56	374.9	94 ± 4	92 ± 5	92	(Tadkaew et al., 2011)
	Amitriptyline	1.57	277.4	86 ± 8	83 ± 7	28 - 98	(Phan et al., 2015; Tadkaew et al., 2011; Wijekoon et al., 2013)
	Naproxen	1.69	230.3	96 ± 4	98 ± 2	36 - 92	(Phan et al., 2015; Tadkaew et al., 2011; Wijekoon et al., 2013)
	Ibuprofen	1.91	206.3	100 ± 0	100 ± 0	90 - 99	(Phan et al., 2015; Tadkaew et al., 2011; Wijekoon et al., 2013)
	Clozapine	2.17	326.8	97± 2	98 ± 1	85	(Tadkaew et al., 2011)
	Gemfibrozil	3.03	250.3	98 ± 3	99 ± 1	33 - 99	(Phan et al., 2015; Tadkaew et al., 2011; Wijekoon et al., 2013)
	Compounds containing only EDG, but having nitrogen-bearing heterocyclic structure and showing moderate removal efficiency						
	Trimethoprim	-0.48	290.3	43 ± 20	42 ± 21	0 - 90	(Phan et al., 2015; Tadkaew et al., 2011)
	Triamterene	0.52	253.3	42 ± 17	43 ± 18	28	(Tadkaew et al., 2011)
	Omeprazole	2.34	345.4	63 ± 14	65 ± 16	62	(Tadkaew et al., 2011)
Log D > 3.2	Phenylphenol	3.29	170.2	100 ± 0	100 ± 0	99%	(Alturki et al., 2012)
	Bisphenol A	3.64	228.3	96 ± 6	97 ± 5	70 - 99	(Phan et al., 2014; Tadkaew et al., 2011)
	Diazinon	3.77	304.4	56 ± 7	59 ± 7	0	(Luo et al., 2014b)
	t-Octylphenol	5.18	206.3	91 ± 6	88 ± 10	45 - 99	(Phan et al., 2015; Tadkaew et al., 2011; Wijekoon et al., 2013)
	Triclosan	5.34	289.5	0 ± 58	82 ± 7	61 - 97	(Phan et al., 2015; Tadkaew et al., 2011; Wijekoon et al., 2013)
	Triclocarban	6.07	315.6	92 ± 3	90 ± 9	56 - 98	(Phan et al., 2015; Tadkaew et al., 2011)
	Nonylphenol	6.14	220.4	99 ± 1	93 ± 6	0 - 99	(Tadkaew et al., 2011)

LIST OF FIGURE CAPTIONS

Figure 1: Schematic diagram of the lab-scale NF-MBR system. PG: pressure gauge; FI: flow indicator.

Figure 2: TOC and TN concentration and removal by NF-MBR. Experimental conditions: HRT of 27 h; $SRT_{estimated}$ > 1000 d; DO concentration of 7 ± 1 mg L^{-1}; pH of 6.0 ± 0.5; and temperature of 21.0 ± 2.6 (average ± standard deviation of 26 measurements).

Figure 3: Concentration and removal efficiency of NH_4^+-N by NF-MBR.

Figure 4: Average removal of the selected TrOCs by NF-MBR. Error bars indicate the standard deviation calculate from triplicate (influent/effluent) or duplicate (supernatant) samples taken once a week for 10 weeks.

Figure 5: Concentration of the selected TrOCs detected in sludge. Error bars indicate standard deviation calculated from 6 measurements.

Figure 6: Fate of TrOCs during NF-MBR treatment.

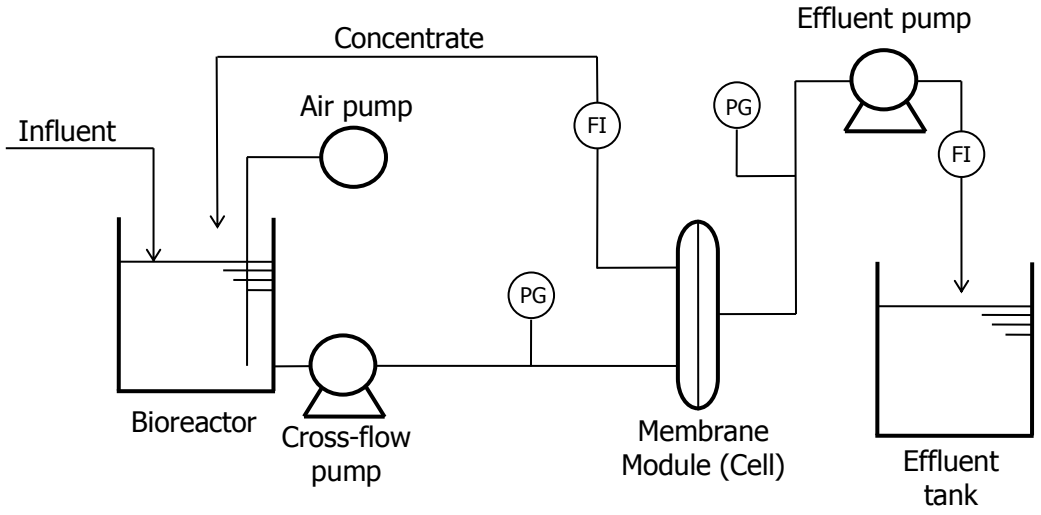
Effluent pump
Concentrate
Air pump
Influent
FI
PG
FI
PG
Bioreactor
Cross-flow
pump
Membrane
Module (Cell)
Effluent
tank

Figure 1

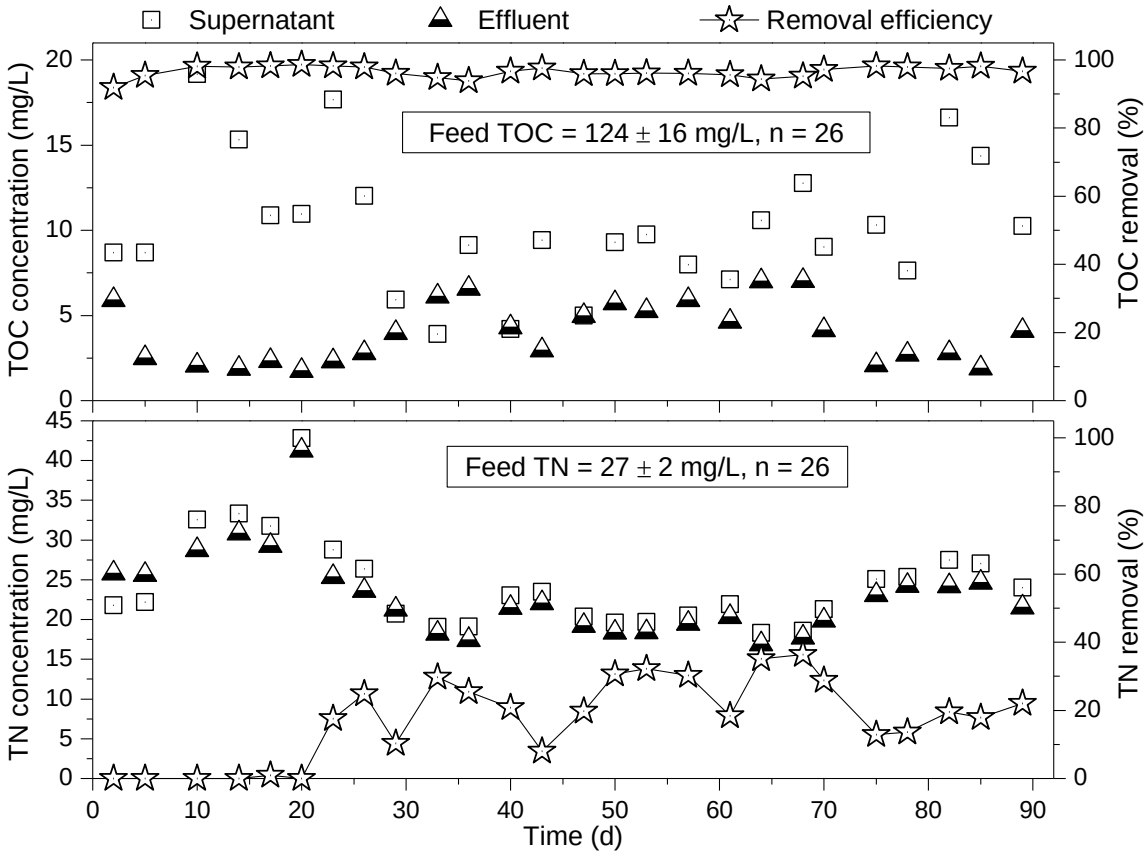
Supernatant
Effluent
Removal efficiency
TOC concentration (mg/L)
TOC removal (%)
Feed TOC = 124 ± 16 mg/L, n = 26
TN concentration (mg/L)
TN removal (%)
Feed TN = 27 ± 2 mg/L, n = 26
Time (d)

Figure 2

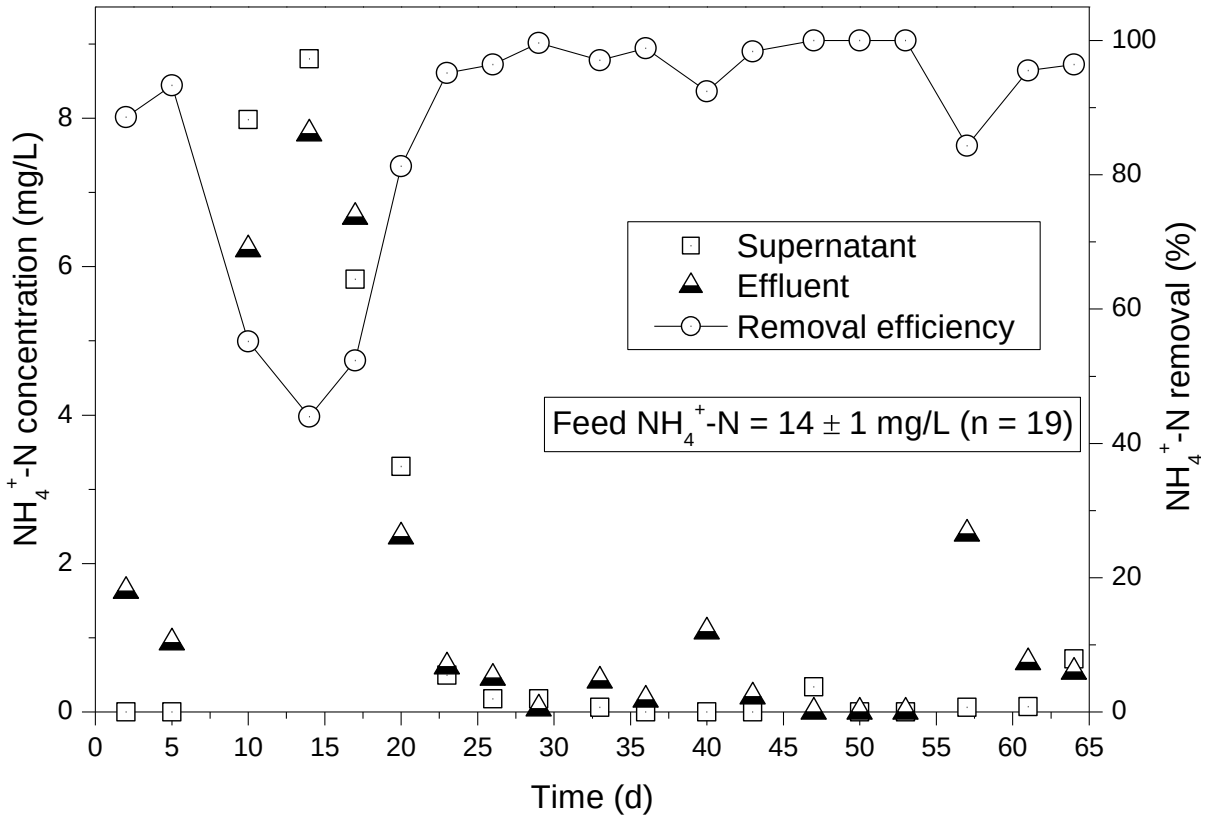
Supernatant
Effluent
Removal efficiency
Feed NH4+-N = 14 ± 1 mg/L (n = 19)
NH4+-N concentration (mg/L)
NH4+-N removal (%)
Time (d)
0
2
4
6
8
0
20
40
60
80
100
0
5
10
15
20
25
30
35
40
45
50
55
60
65

Figure 3

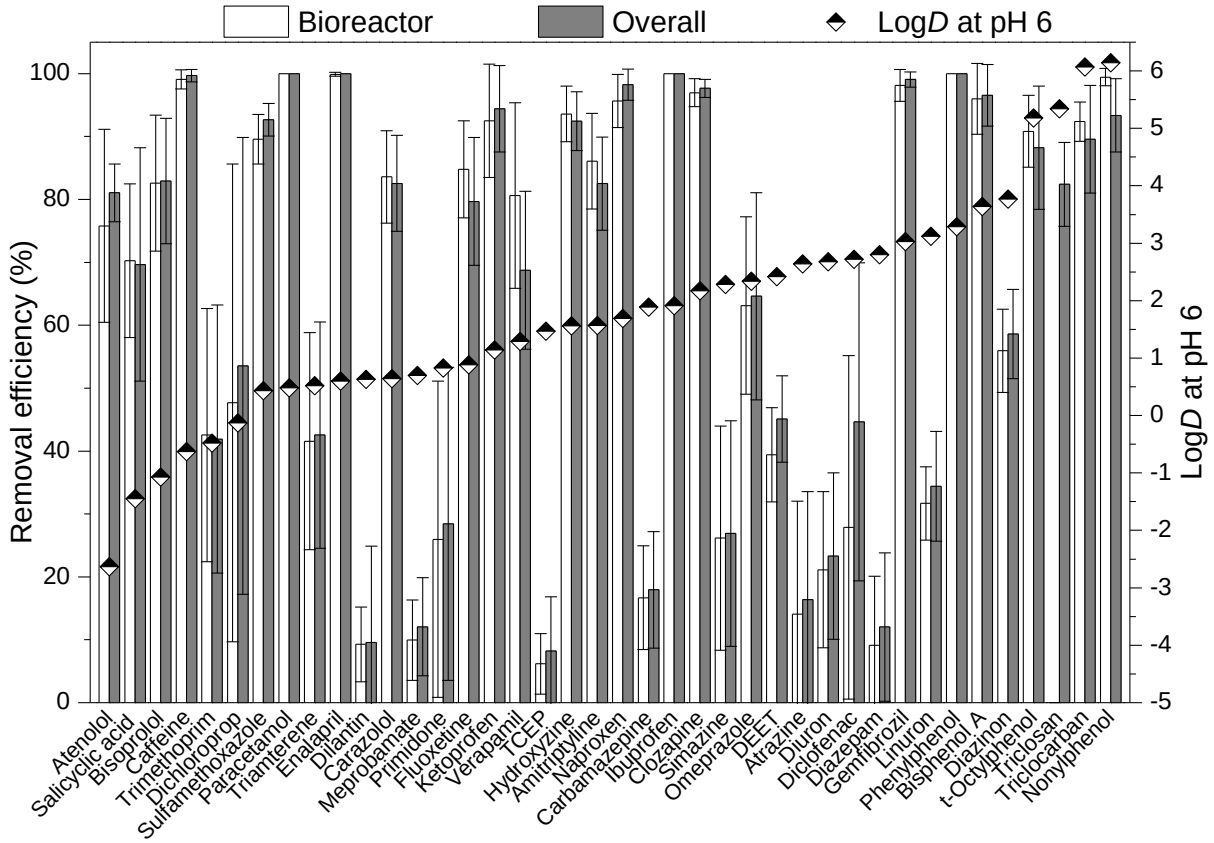
Bioreactor
Overall
LogD at pH 6
Removal efficiency (%)
LogD at pH 6
Atenolol
Salicylic acid
Bisoprolol
Caffeine
Trimethoprim
Dichloroprop
Sulfamethoxazole
Paracetamol
Triamterene
Enalapril
Dilantin
Carazolol
Meprobamate
Primidone
Fluoxetine
Ketoprofen
Verapamil
TCEP
Hydroxyzine
Amitriptyline
Naproxen
Carbamazepine
Ibuprofen
Clozapine
Simazine
Omeprazole
DEET
Atrazine
Diuron
Diclofenac
Diazepam
Gemfibrozil
Linuron
Phenylphenol
Bisphenol A
Diazinon
t-Octylphenol
Triclosan
Triclocarban
Nonylphenol

Figure 4

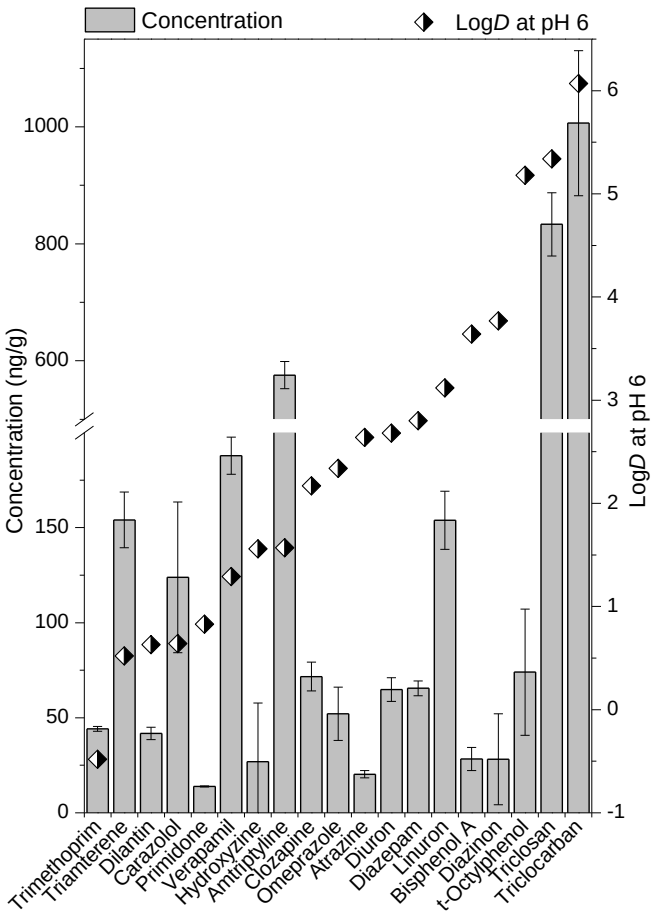
Concentration
LogD at pH 6
Concentration (ng/g)
LogD at pH 6
0
50
100
150
600
800
1000
-1
0
1
2
3
4
5
6
Trimethoprim
Triamterene
Dilantin
Carazolol
Primidone
Verapamil
Hydroxyzine
Amitriptyline
Clozapine
Omeprazole
Atrazine
Diuron
Diazepam
Linuron
Bisphenol A
Diazinon
t-Octylphenol
Triclosan
Triclocarban

Figure 5

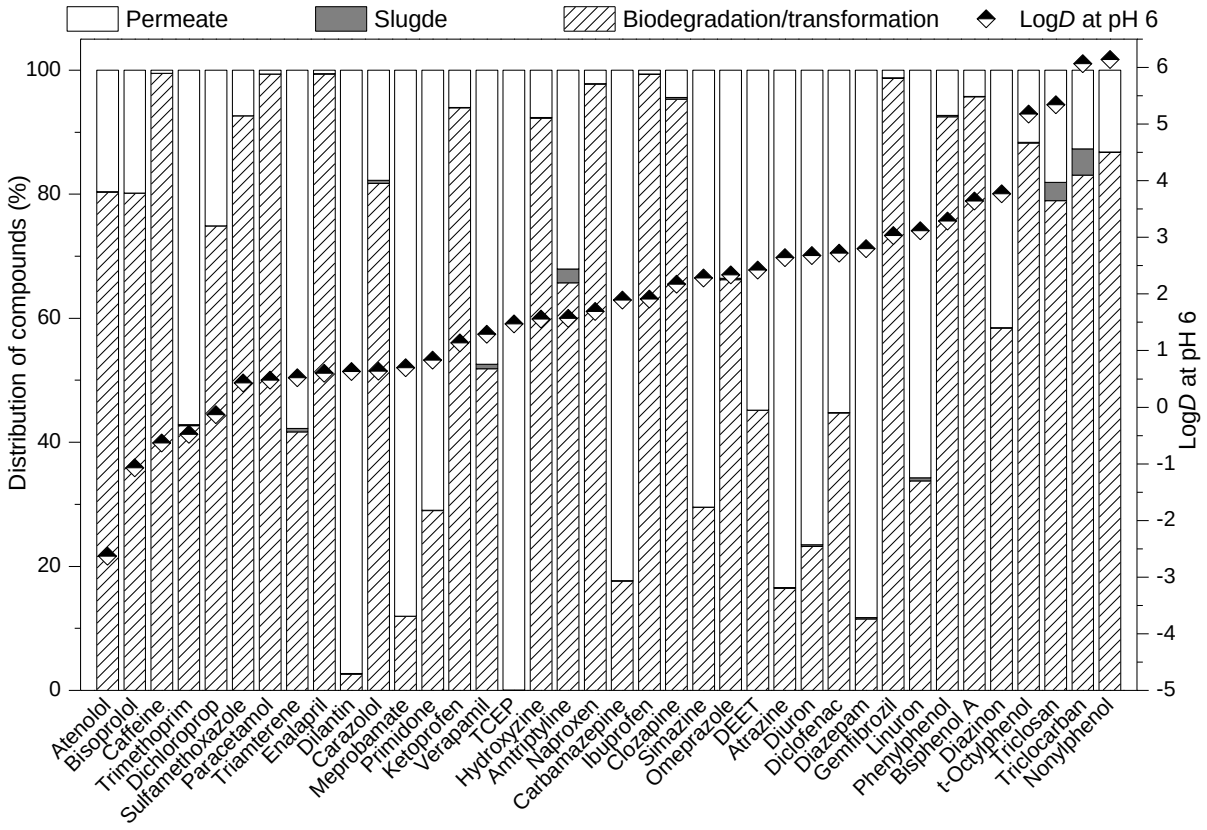
Permeate
Slugde
Biodegradation/transformation
LogD at pH 6
Distribution of compounds (%)
LogD at pH 6
100
80
60
40
20
0
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
Atenolol
Bisoprolol
Caffeine
Trimethoprim
Dichloroprop
Sulfamethoxazole
Paracetamol
Triamterene
Enalapril
Dilantin
Carazolol
Meprobamate
Primidone
Ketoprofen
Verapamil
TCEP
Hydroxyzine
Amitriptyline
Naproxen
Carbamazepine
Ibuprofen
Clozapine
Simazine
Omeprazole
DEET
Atrazine
Diuron
Diclofenac
Diazepam
Gemfibrozil
Linuron
Phenylphenol
Bisphenol A
Diazinon
t-Octylphenol
Triclosan
Triclocarban
Nonylphenol

Figure 6